

C1 subsequent polymerization or grafting reactions. This oversight in the prior art is reflective of the fact that the invention of POSS-based reagents, monomers and polymer technology has only recently been developed and consequently post-dates this prior art. Hence POSS compositions and processes relevant to the types of systems desired for POSS monomer/polymer technology were not envisioned in the prior art. Additionally the prior art does not demonstrate the action of bases on silane, silicate, or silsesquioxane feedstocks suitable for producing low-cost and high purity POSS systems.--

Please replace the paragraph beginning at page 2, line 18, with the following rewritten paragraph:

C2 --In contrast to the prior art (see, e.g., Brown, J.F., Vogt, L.H., and P.I. Prescott J., Am. Chem. Soc. 1964, 86, 1120-1125; Marsmann, H.C. and Rilowski, E., Polyhedron, 1997, 16, 3357-3361), the processes taught here specifically enable the development of lower cost, high purity POSS systems bearing functionalities useful as derivitizable chemical reagents and feedstocks.--

Please delete the words [Figure 1. Examples of Common Silsesquioxane, Silicate, POSS Nanostructures and Fragments.] on page 5, top of the page.

Please replace "Figure 2. Illustration of Process I where polymeric silsesquioxane resins are converted into POSS fragments and nanostructures." on page 9, top of the page, with --Scheme 1--.

Please replace the paragraph beginning at page 9, line 1, with the following rewritten paragraph:

SUB  
D2  
C3 --For the above reaction scheme (Scheme 1) the polymeric silsesquioxane resin is converted into either POSS fragments or nanostructured POSS cage species depending on the type of base and conditions employed. The conversion of polysilsesquioxanes  $[\text{RSiO}_{1.5}]_{\infty}$  to POSS-species (homoleptic  $[(\text{RSiO}_{1.5})_n]_{\Sigma\#}$ , functionalized homoleptic  $[(\text{RSiO}_{1.5})_m(\text{RXSiO}_{1.0})_n]_{\Sigma\#}$ , heteroleptic  $[(\text{RSiO}_{1.5})_m(\text{RSiO}_{1.5})_n]_{\Sigma\#}$  and functionalized heteroleptic  $[(\text{RSiO}_{1.5})_m(\text{RXSiO}_{1.0})_n]_{\Sigma\#}$ ) or into POSS-fragments  $[(\text{RXSiO}_{1.5})_n]$  can be selectively controlled through manipulation of the process variables discussed above. The process can be conducted using a polysilsesquioxane resin which may contain only one type of R group to produce homoleptic  $[(\text{RSiO}_{1.5})_n]_{\Sigma\#}$  products. Alternatively the process can be

C3

carried out using polysilsesquioxane resins containing more than one type of R group or with mixtures of polysilsesquioxanes in which each contains different R groups to afford heteroleptic  $[(\text{RSiO}_{1.5})_m(\text{R}'\text{SiO}_{1.5})_n]_{\Sigma\#}$  products. For the above reaction scheme (Scheme 1) in which mixtures of homoleptic POSS cages (i.e. R of one POSS cage  $\neq$  R of the second POSS cage) are substituted for the polysilsesquioxane resin the process effectively converts mixtures of homoleptically substituted POSS cages into heteroleptic POSS cages (functionalized and nonfunctionalized) that contain statistical distributions of different R groups per cage. In most cases the POSS fragments and various homo or heteroleptic nanostructured POSS species can be separated from one another through crystallization, or extractions by utilizing the differences in solubility between the reaction products and the starting silsesquioxane.--

Please replace the paragraph beginning at page 10, line 8, with the following rewritten paragraph:

C4

--The process developed utilized bases (as defined previously) to convert fragments and functionalized POSS nanostructures  $[(\text{RSiO}_{1.5})_m(\text{RXSiO}_{1.0})_n]_{\Sigma\#}$  into alternate functionalized POSS nanostructures  $[(\text{RSiO}_{1.5})_m(\text{RXSiO}_{1.0})_n]_{\Sigma\#}$ . In the process a POSS fragment is dissolved or suspended in acetone, benzene or alcoholic solvents after which a solution of base is added with stirring. In general the reaction conditions employed in this process are milder than those used in Process I and can utilize both hydroxide and nonhydroxide bases, while the molar ratio of base relative to silicon is 1:10 (with 1:1 or 1:2 ration being preferred). Scheme 2 below illustrates some examples of the conversion of POSS fragments into POSS cages.--

Please replace the paragraph "Figure 3. POSS Fragments converted into POSS cages." at the bottom of page 10 with --Scheme 2--.

Please replace the paragraph beginning at page 11, line 8, with the following rewritten paragraph:

C5

--When mixtures of POSS fragments are utilized they are incorporated statistically into the POSS structure and their final composition is based on the stoichiometry of the starting POSS fragments. In some cases the statistical degree of substitution between these groups is governed by isomorphism resulting from the nearly identical topological shape of the R group (e.g. vinyl and ethyl). Isomorphic governance is often observed for closely

C5  
related R groups (e.g. allyl and propyl etc.); however, on occasion the trend is not followed due to other factors such as rate of reaction, reagent addition, or solubility between various POSS fragments and products. For example the reaction of 1 equivalent of EthylundeconoateSi(OMe)<sub>3</sub> or VinylSi(OMe)<sub>3</sub> with 7 equivalents of MeSi(OMe)<sub>3</sub> results in a molecule of formula 2 of the composition [(ViSiO<sub>1.5</sub>)<sub>1</sub>(MeSiO<sub>1.5</sub>)<sub>7</sub>]<sub>Σ8</sub> or [(EthylundeconoateSiO<sub>1.5</sub>)<sub>1</sub>(MeSiO<sub>1.5</sub>)<sub>7</sub>]<sub>Σ8</sub> despite the topological dissimilarity between the R groups.--

Please replace the paragraph beginning at page 11, line 27, with the following rewritten paragraph:

SUB  
D3  
C6  
--Scheme 3 illustrates actual reactions that use the conditions described in Process II as proof that the bases and conditions described in Process II are effective for the conversion of functionalized POSS cages (i.e. [(RSiO<sub>1.5</sub>)<sub>m</sub>(RXSiO<sub>1.0</sub>)<sub>n</sub>]<sub>Σ#</sub>) desired POSS structures. It should also be noted that in most cases this process results in an increase in the number of functionalities (X) on a POSS nanostructure while at the same time maintaining the original number of silicon atoms contained within the starting nanostructural framework. This can be desirable for a variety of subsequent synthetic product manipulations and derivations.--

Please delete the paragraph beginning at page 11, line 34.

Please replace the paragraph "Figure 4. POSS Cages being interconverted." at the middle of page 12, after the two reaction schemes, with --Scheme 3--.

Please replace the paragraph beginning at page 12, line 1, with the following rewritten paragraph:

C7  
--The first example in Scheme 3 illustrates the selectivity for the cleavage of 6 membered silicon-oxygen rings in the presence of 8 membered silicon-oxygen rings by the base, to afford the trifunctionalized POSS species. This reaction is driven by the release of greater ring strain energy from the cleavage of the 6 membered silicon-oxygen ring vs. cleavage of the 8 membered silicon-oxygen ring and is thermodynamically favorable. In the second example the energy of the twisted conformation is relieved upon cleavage to form a more open structure.--

Please replace the paragraph "Figure 5. Silsesquioxane/siloxane fragments being inserted into POSS Cages." at the top of page 14, after the two reaction schemes, with --Scheme 4--.

Please replace the paragraph beginning at page 14, line 1, with the following rewritten paragraph:

C8 --Scheme 4 above illustrates examples of Silsesquioxane/siloxane fragments being inserted into POSS cages. The net reaction in the examples shown in Scheme 4 is cleavage of an Si-O-Si bond in the POSS or POSS silicate nanostructure and insertion of the POSS fragment. This reaction results in the expansion of the silicon-oxygen ring in the POSS nanostructured product. Note that the ring expansion in these reactions is in some cases favored thermodynamically through relief of ring strain in the silsesquioxane starting material. For example, the reaction of 1 equivalent of Vinyl(OMe)<sub>3</sub> with  $[(c-C_6H_{11})SiO_{1.5}]_6$  results in POSS molecule having the composition  $[(c-C_6H_{11}(SiO_{1.5})_4(c-C_6H_{11})(HO)SiO_{1.0})_2(ViSiO_{1.0})_1]_{\Sigma 7}$ .--

Please replace the paragraph beginning at page 15, line 8, with the following rewritten paragraph:

C9 --Homoleptic POSS nanostructures  $[(RSiO_{1.5})_n]_{\Sigma n}$  are readily converted into POSS nanostructures having the formula  $[(RSiO_{1.5})_m(RXSiO_{1.0})_n]_{\Sigma n}$ , as well as POSS fragments having the formula  $RSiX_3$ ,  $[(RXSiO_{0.5})_n]$ ,  $[(RXSiO_{1.0})_n]$ , or  $[(RSiO_{1.5})_m(RXSiO_{1.0})_n]$  through the use of bases as shown in Scheme 5. Note that all possible geometric and stereochemical isomers for each product are not shown.--

Please replace the paragraph "Figure 6. Illustration of Process III" on page 15, toward the bottom of the page and after the three reaction schemes, with --Scheme 5--.

Please replace the paragraph beginning at page 15, second line 1 at the bottom of the page, with the following rewritten paragraph:

C10 --Furthermore as a variation of this process it is possible to interconvert various sizes of POSS nanostructures. For example, with the proper addition of base  $[(RSiO_{1.5})_6]_{\Sigma 6}$  can be either cleaved into a smaller POSS fragments (e.g.  $RSiX_3$ ,  $[(RXSiO_{0.5})_n]$ ,  $[(RXSiO_{1.0})_n]$ , or  $[(RSiO_{1.5})_m(RXSiO_{1.0})_n]$ ) or functionalized into heteroleptic POSS nanostructures of the same

C10

size (e.g.  $[(\text{RSiO}_{1.5})_4(\text{RXSiO}_{1.0})_2]_{\Sigma 6}$ ) or larger (e.g.  $[(\text{RSiO}_{1.5})_4(\text{RXSiO}_{1.0})_3]_{\Sigma 7}$ ) as shown in Scheme 6.--

Please replace the paragraph "Figure 7. Illustration of Process III" at the middle of page 16 with --Scheme 6--.

Please replace the paragraph beginning at page 16, second line 1 toward the end of the page, with the following rewritten paragraph:

C11

--As a variation of the above it is recognized that this process can utilize mixtures and distributions of POSS cages as well as polyhedral oligomeric silicate species (e.g.  $[(\text{CH}_3)_3\text{SiO}]\text{SiO}_{1.5}]_6$ ,  $[(\text{CH}_3)_4\text{NO}]\text{SiO}_{1.5}]_6$ ,  $[(\text{CH}_3)_3\text{SiO}]\text{SiO}_{1.5}]_8$ ,  $[(\text{CH}_3)_4\text{NO}]\text{SiO}_{1.5}]_8$ ). In such cases the base effectively converts cages of several sizes into functionalized and nonfunctionalized heteroleptic POSS nanostructures as shown in Scheme 7. This represents an entirely new synthetic route for the preparation of the very useful incompletely condensed trisilanol reagents  $[(\text{RSiO}_{1.5})_4(\text{RXSiO}_{1.0})_3]_{\Sigma 7}$  in particular where X = OH.--

Please replace the paragraph "Figure 8. Illustration of the conversion of POSS and Silicate Nanostructures - Process III" on page 17, before line 1, to --Scheme 7--.

Please replace the paragraph beginning at page 17, line 1, with the following rewritten paragraph:

C12

--A final variation of this process is the selective action of base on heteroleptic POSS nanostructures (see Scheme 8). POSS nanostructures bearing more than one type of R group per cage  $[(\text{RSiO}_{1.5})_m(\text{RSiO}_{1.5})_n]_{\Sigma \#}$  are readily converted through the use of base into functionalized POSS nanostructures  $[(\text{RSiO}_{1.5})_m(\text{RXSiO}_{1.0})_n]_{\Sigma \#}$ . Note that all possible geometric and stereochemical isomers are not shown.--

Please replace "Figure 9. Illustration of the conversion of POSS Nanostructures - Process III" at the bottom of page 17 to --Scheme 8--.

Please replace the paragraph beginning at page 18, line 18, with the following rewritten paragraph: